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ARL-RP-184

July 2007

A reprint from the Proceedings of the SAMPE 2007 Conference, Baltimore, MD, 3–7 June 2007.

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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) July 2007		2. REPORT TYPE Reprint		3. DATES COVERED (From - To) January 2006–February 2007	
4. TITLE AND SUBTITLE High Performance Fatty Acid-Based Vinyl Ester Resin for Liquid Molding				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Xing Geng, * John J. La Scala, James M. Sands, and Giuseppe R. Palmese*				5d. PROJECT NUMBER 789531	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRD-ARL-WM-MC Aberdeen Proving Ground, MD 21005-5066				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-RP-184	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES A reprint from the <i>Proceedings of the SAMPE 2007 Conference</i> , Baltimore, MD, 3–7 June 2007. *Department of Chemical Engineering, Drexel University, Philadelphia, PA 19104					
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15. SUBJECT TERMS fatty acid, low-VOC, styrene emission, vinyl ester, liquid molding					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 16	19a. NAME OF RESPONSIBLE PERSON John J. La Scala
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (Include area code) 410-306-0687

HIGH PERFORMANCE FATTY ACID-BASED VINYL ESTER RESIN FOR LIQUID MOLDING

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ABSTRACT

Liquid resins used for molding composite structures are a significant source of volatile organic compounds (VOC) and hazardous air pollutant (HAP) emissions. One effective method of reducing styrene emissions from vinyl ester (VE) resins is to replace some or all of the styrene with fatty acid-based monomers. In our investigation, the styrene was reduced to 20-25 wt% compared to 40-60 wt% associated with commercial products. In addition, fatty acid-based monomers can bring about other benefits like higher toughness, lower exothermal heat and low volume shrinkage. One disadvantage of fatty acid-based VE resins, however, is the reduction in glass transition temperature (T_g) which limits their use in high temperature environments. Therefore, the specific focus of this work was to design high T_g fatty acid-based VE resins with low viscosities and high fracture properties. These high T_g resins were designed by blending fatty acid monomers with novolac vinyl esters. Various low viscosity formulations were established with T_g s as high as 147°C. Moreover, approaches to further improve the fracture toughness of the resin were investigated. Vinyl terminated poly(butadiene-*co*-acrylonitrile) (VTBN) and epoxy terminated poly(butadiene-*co*-acrylonitrile) (ETBN) were used as modifiers to these fatty acid vinyl ester resins. Compared with commercial novolac VE resin, marked improvement in fracture toughness (167 J/m² versus 56 J/m²) was achieved.

KEYWORDS: Styrene Emission, Vinyl Ester, Liquid Molding

1. INTRODUCTION

Vinyl esters (VE) are one of the most popular resin systems used in polymer matrix composite fabrication for military and commercial applications due to their good properties, low weight and low cost. However, current commercial VE resins generally contain a high concentration of styrene to provide low viscosities suitable for composite fabrication via inexpensive liquid transfer molding techniques. Styrene is a hazardous air pollutant (HAP) and a volatile organic compound (VOC), and its use in composite manufacturing is being limited by the Federal Environmental Protection Agency of the United States of America [1]. Accordingly, fatty acid monomers have been developed and used to replace styrene in VE resins because of their low cost, low volatility, and the fact that they are derived from renewable resources. These monomers allow for the production of high performance composites while using ~20 wt% styrene, compared to 40-60 wt% styrene associated with commercial products [2,3]. Additionally, the use of fatty acid monomers in VE resins can result in other beneficial properties, such as high toughness, low exothermal heat and low volume shrinkage.

One disadvantage associated with the use of fatty acid monomers as reactive diluents to partially or fully replace styrene however, is the low T_g (below 0°C) of their homopolymers compared with that of styrene (~100°C) which limits their use in producing VE resins for high temperature applications. The use of multifunctional novolac VE resins was explored to partially counteract the loss of T_g resulting from fatty acid monomers and to produce high temperature low VOC VE resins. Aside from their high styrene content (33%) relative to fatty acid-based vinyl esters, commercial multifunctional novolac VE systems, such as Derakane 470-300 and 470HT-400, possess low fracture toughness due to their high crosslink densities. Though the presence of fatty acid can lessen this problem to some extent, other effective modifiers have to be employed to improve the fracture toughness to a higher level.

Alternatively, the addition of liquid rubber can be employed to improve the fracture toughness of VE resins [4-7]. Vinyl terminated poly(butadiene-*co*-acrylonitrile) (VTBN) and epoxy terminated poly(butadiene-*co*-acrylonitrile) (ETBN) exhibit significant improvement in certain VE resins, provided that the liquid rubber can form a miscible system with VE monomers and will precipitate completely from the resins resulting in a second phase after cure [4].

The goal of this study is to make low VOC high performance VE resins by using fatty acid to modify current commercial novolac VE resins. Ideally, the resulting resins will have low viscosities suitable for liquid molding, wet T_gs over 120°C, and fracture properties double that of commercial novolac VE resins.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

2.1 Materials Derakane 470HT-400 vinyl ester resin was obtained from Ashland and was used without modification. Epon Resin 160, a novolac epoxy, and Epon 828, a diglycidyl ether of bisphenol A (DGEBA), were purchased from Hexion Specialty Chemicals and was used to synthesize vinyl ester resins. Methacrylic acid was purchased from Aldrich chemicals and was reacted with the epoxy monomers to produce vinyl ester. Two commercial DGEBA vinyl ester resins with $n \sim 0.1$ and containing no styrene, CN 151 and RDX 26936, were obtained from Sartomer and Cytec Surface Specialties Inc., respectively. Methacrylated octanoic acid (MOct) was produced by Applied Poleramic, Inc. and was used without modification. The liquid rubbers used for the toughening study were vinyl terminated poly(butadiene-*co*-acrylonitrile) (Hycar 1300×33) and epoxy terminated poly(butadiene-*co*-acrylonitrile) (Hycar 1300×40) provided by Noveon Solutions.

2.2 Vinyl Ester Resins Preparation Vinyl ester monomers were prepared by reacting methacrylic acid with Epon 160 ($n=0.5$) and Epon 828 ($n=0.098$) to produce VE 160 and VE 828, respectively (Figure 1). The reaction was catalyzed by 1 wt% AMC-2 (Aerojet Chemicals, Rancho Cordova, CA), which is a mixture of 50% trivalent organic chromium complexes and 50% phthalate esters. In order to maintain stability and prevent gelation, 0.01 wt% or 100 ppm hydroquinone was added as an inhibitor. Acid number below 4 and disappearance of the epoxy peak, as seen through Fourier transform infrared spectroscopy (917cm^{-1}), are two indicators for the end of the reaction. Typically, the reaction was allowed to proceed for 2 hours and a green liquid product was obtained.

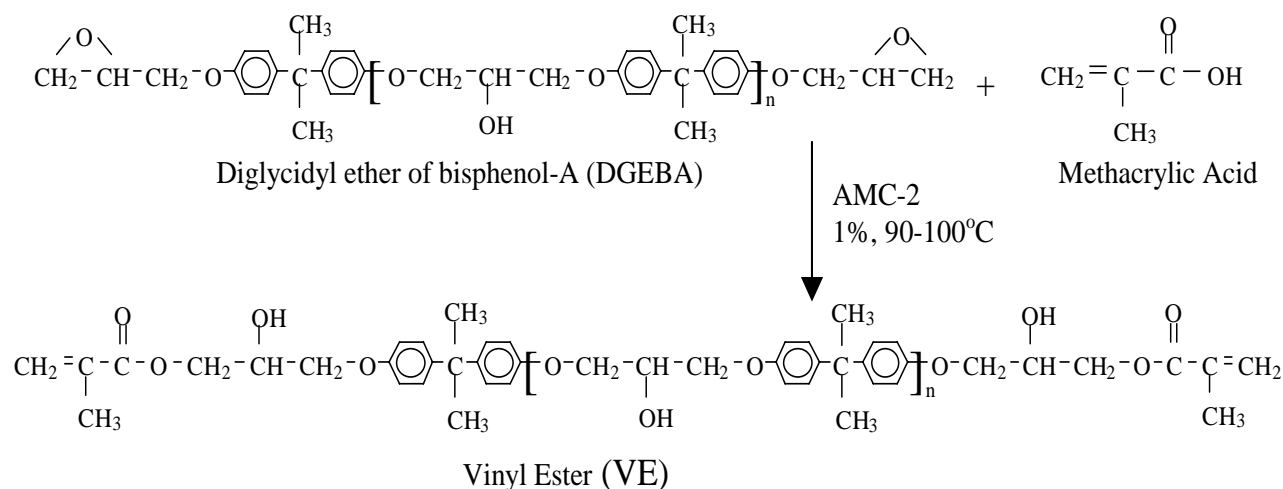


Figure 1: The reaction of DGEBA and methacrylic acid to produce the vinyl ester

2.3 Room Temperature Cure of VE Resins VE resin systems were initiated using Trigonox 239A (Akzo Nobel Chemicals, Chicago, IL), containing 45% cumene hydroperoxide, and cobalt naphthenate (CoNap) (Aldrich) as a catalyst to promote room temperature cure. The Trigonox and CoNap masses used were 1.5% and 0.375%, respectively, of the total resin mass. All resins were allowed to cure at room temperature for 16h. Fracture toughness samples were post-cured at 130°C for 2 h.

2.4 Procedures Dynamic mechanical analysis (DMA) was performed using a TA instruments DMA 2980 at a frequency of 1 Hz and at a heating rate of 2°C/min. Specimens of dimensions 30×12×3 mm³ were tested in single cantilever beam loading configuration.

For the water absorption study, samples with dimensions 30×12×1.5 mm³ were exposed to controlled humidity environments until saturation was reached. Samples were placed 60°C environments with a relative humidity (RH) of 79%. Samples were also immersed in boiling water for 24 hrs. The samples at 60°C and 79% RH were periodically removed from the environments and superficially dried. The samples were weighed to determine the amount of water absorption, and then re-introduced to the humid environment. Saturation was achieved when the sample weight no longer changed with exposure time.

Fourier Transform Infrared Spectroscopy (FTIR) was also used to monitor the water absorption of samples. A Thermo Nicolet Nexus 670 FTIR spectrometer was used. Near IR spectroscopy was conducted in a transmission mode at 16 cm⁻¹ with 32 scans per data point. The water-saturated samples were also tested via DMA to determine the effect of water absorption on Tg.

The viscosities of designed resin systems were evaluated using a Brookfield digital viscometer. The viscosity measurement was taken at 30°C.

3. RESULTS AND DISCUSSION

3.1 Design of High Tg Formulation Fatty acid based resin with dry Tg of 140°C and wet Tg of 120°C is required for certain DoD applications. With this aim, novolac vinyl esters with

multiple functional groups were employed in this study to improve the Tg of fatty acid based resins. Consequently, Derakane 470HT-400 (simplified as Der470HT in this study) was selected because it has the highest Tg among the commercial available VE resins. The goal was to reduce the styrene content in this resin from 33 wt% to 25 wt% or less by replacing styrene with methacrylated octanoic acid, while achieving good performance and processibility. To compensate for the loss of vinyl ester monomer when reducing the amount of styrene, DGEBA based vinyl ester (VE 828) was added to the system. As summarized in Table 1, formulations were designed by adjusting the weight fraction of MOct and Styrene in order to achieve both the performance and processibility at the minimum loading amount of styrene. As can be seen, the formulation of 75.8 wt% Der 470HT, 14.2 wt% VE 828 and 10 wt% MOct gave the highest Tg (147°C) as well as the lowest viscosity (388 cP at 30°C). Because of the excellent properties of this resin, it will be evaluated throughout this paper and abbreviated as FAVE-O-470HT. A representative DMA scan is shown in Fig. 2. The material is in the glassy state at low temperatures, goes through a glass transition at moderate temperatures, and is a rubber at high temperatures. The storage modulus monotonically decreases with temperature, while the loss modulus goes through a maximum. The temperature at which the maximum in the loss modulus occurs was considered the Tg of the material.

Table 1: Representative formulations of VE resins

Formulation No.	Der470HT (wt%)	VE828 (wt%)	MOct (wt%)	Tg (°C) Actual	Styrene (wt%)
1	60.6	29.4	10	147	20
2	60.6	24.4	15	138	20
3	75.8	14.2	10	147	25
4	75.8	9.2	15	136	25

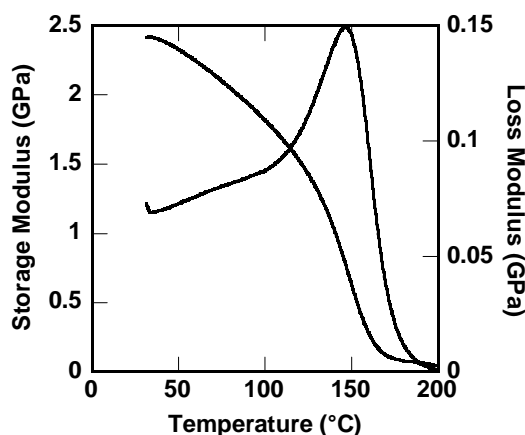


Figure 2: Dynamic mechanical spectrum of the system of 75.8 wt.% Der470HT 14.2 wt.% VE828 and 10 wt.% MOct.

Table 2: Viscosity of designed resins compared with commercial VE resins

Resin	Viscosity (cP) at 30°C
Design 1	780
Design 2	540
Design 3	388
Design 4	296
Der 470HT	290
FAVE-O-470HT *	392

* CN151 was used instead of VE 828

3.3 Water Absorption Study Two different conditions, boiling water for 24 h and 60°C water vapor with humidity as 79% until saturation, were employed in this study to determine the effect of moisture on the thermomechanical properties of fatty acid-based resins. A representative VE resin system of VE 160/MOOct/St (70-5-25) was investigated with respect to water absorption and its influence on T_g. The typical DMA results under 100°C water uptake for 24 h are given in Figure 3. T_gs before and after water uptake are 152°C and 133°C respectively which means water uptake will impart a 19°C decrease in T_g. However, the second and third DMA runs of water absorbed sample (Figure 4), demonstrate that the T_g recovers completely after full removal of water, which indicated no hydrolysis occurred during water absorption of VE resins. DMA spectra of sample exposed to 60°C water vapor for 5 days are shown in Figure 5 and 6, and similar results were obtained.

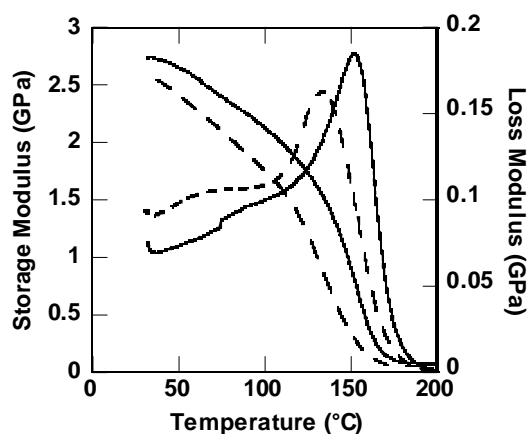


Figure 3: DMA scans of the system of VE 160/MOOct/St (70-5-25) before (solid) and after (dashed) water uptake in 100°C for 24 hours.

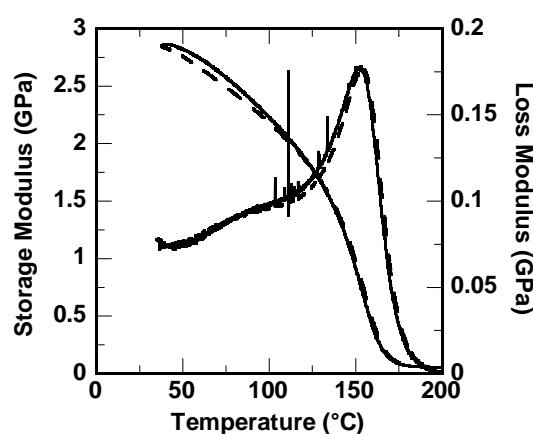


Figure 4: Second (solid) and third (dashed) DMA uptake sample gave T_gs as 152°C and 154°C.

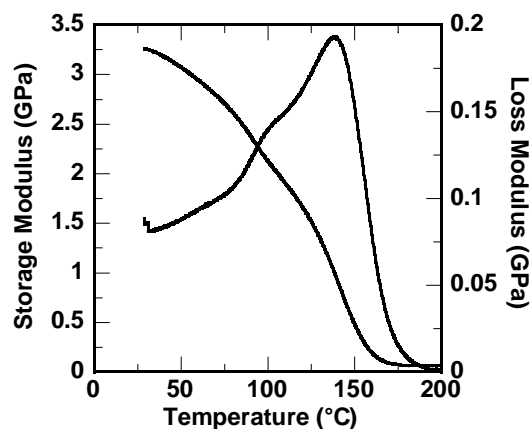


Figure 5: DMA scans of the system of VE 160/MOOct/St (70-5-25) after water uptake at 60°C with RH=79% for 5 days. Resulting sample Tg is 138°C.

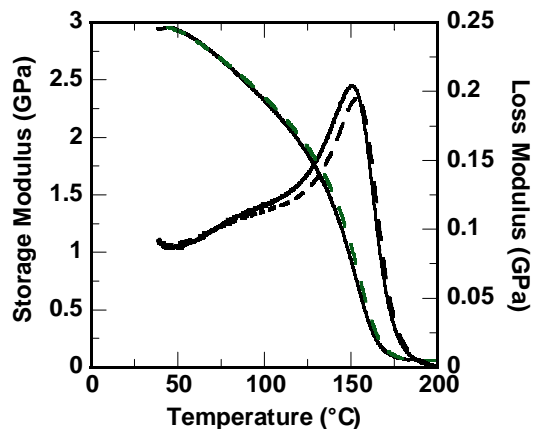


Figure 6: Second (solid) and third (dashed) DMA scans of water uptake sample gave Tgs as 151°C and 153°C.

Near infrared (NIR) spectroscopy was employed to monitor the water uptake of the sample exposed to 60°C during consecutive 7 days with spectra shown in Figure 7. Results show a marked increase in the water peak at $\sim 5100\text{ cm}^{-1}$. No other changes were observed, and the material is unchanged according to NIR after complete water removal. The NIR results also show that after DMA runs, the water can be fully removed as reflected in the disappearance of water peak in NIR spectra (Figure 8).

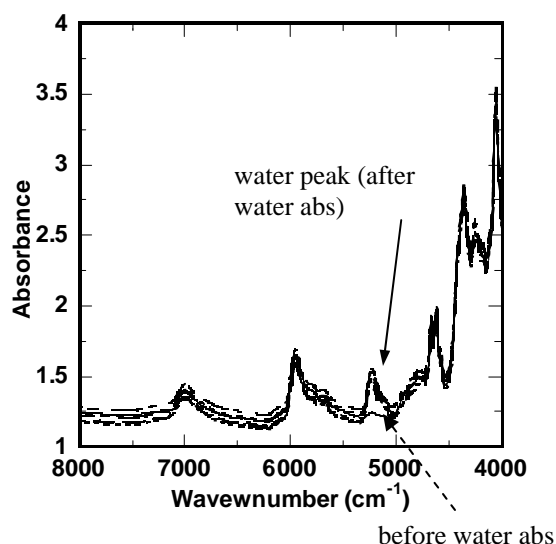


Figure 7: NIR spectra of the system of VE 160/MOOct/St (70-5-25) before and after water uptake in 60°C (RH=79%) for 7 days.

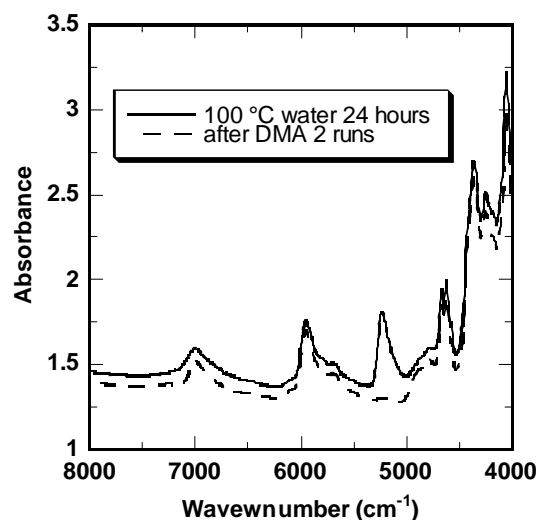


Figure 8: NIR spectra of the sample after water uptake in 100°C for 24 hours and after DMA runs.

The weight gain during the water absorption experiments at 60°C (RH=79%) is shown in Figure 9. It is seen that after 5 days, the water saturation status is reached; the ultimate water absorption percentage is 1.74%. Weight change for a formulation containing 75 wt% VE 160, 5 wt% MOct, and 25 wt% styrene is given in Table 3. Water absorption percentage for 100°C after 24 h and 60°C (RH=79%) after 5 days are 2.25% and 1.62% respectively. These results show that the sample at 100°C will absorb more water and will be correspondingly subject to greater loss in Tg. Accordingly, it can be deduced that water uptake at 100°C for 24 h is a more critical criterion to evaluate the VE resins' resistance to water. The wet Tg of some commercial VE resins were thus measured based on this criterion along with our designed resin system and the results are given in Table 4. The FAVE-O-470HT resin has a moderate wet Tg of 124°C relative to the commercial resins. The Tg is above the goal value of 120°C.

Table 3: The relation between water absorption and Tgs of a formulation containing 75 wt% VE 160, 5 wt% MOct, and 25 wt% styrene.

75VE160-5MOct-25St	Initial	100°C water 24 h	after 1 st run	after 2 nd run	60°C water 5 days	after 1 st run	after 2 nd run
Tg (°C)	152	133	152	154	138	151	153
Sample	0.5812	0.5943	0.578	0.5778			
Weight (g)	0.5930				0.6026	0.5913	0.5911

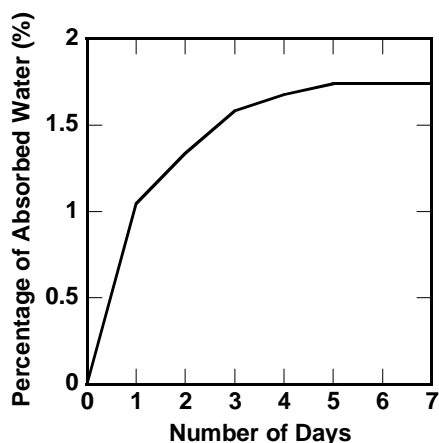


Figure 9: Weight change of sample in 60°C At 79% relative humidity for 7 days

Table 4: Wet Tg of designed resin and commercial VE resins

Resin	Wet Tg after 100°C 24 h (°C)
Derakane 8084	103
Derakane 441-400	125
Derakane 470-300	139
Der 470HT	155
FAVE-O-470HT	124

3.4 Commercial Resin Selection As reported in the previous section, FAVE-O-470HT resin was formulated by blending Derakane 470HT-400 with VE 828, and MOct. This resin has excellent properties, but uses a vinyl ester that is only prepared at the laboratory bench scale. To meet DoD and commercial applications, we must identify the appropriate commercial VE monomer resin as a replacement for VE 828. CN151 and RDX 26929, both of them based on methacrylated diglycidyl ether of bisphenol A epoxy resin, were consequently investigated with regard to their impact on Tg and other properties. Though both of these two resins can produce FAVE-O-470HT resin with slightly different Tg properties (~145°C), when mixed with 33% styrene respectively, the RDX 26939 monomer produced a resin with a significantly higher Tg

(153°C) than the CN151-based resin (132°C), as illustrated in Figure 10 and 11. The difference in T_g properties of these two resins is likely due to lower methacrylate functionality in CN-151.

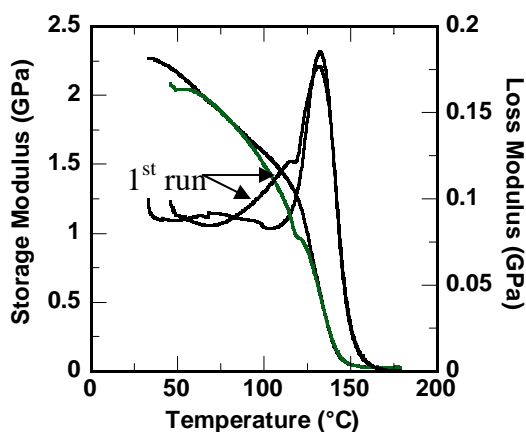


Figure 10 DMA spectra for CN151 with 33% Styrene. T_g of 1st run is 132°C, T_g of 2nd run is 132°C. Fully cure was achieved by heating at 90°C for several days heating.

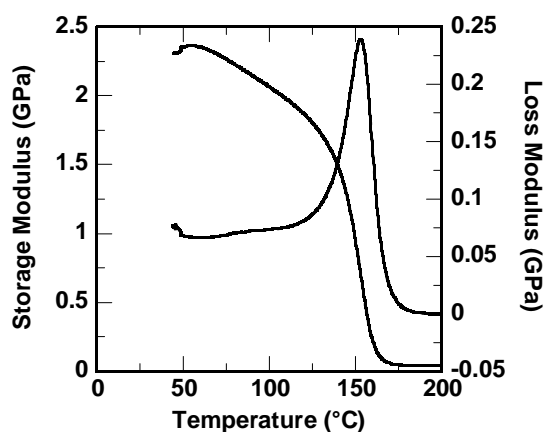


Figure 11 DMA spectrum of sample of RDX 26939 with 33% Styrene. T_g of 153°C shows up in the second run.

3.5 Fracture Toughness Improvement 5% and 10% weight fraction of vinyl terminated poly(butadiene-*co*-acrylonitrile) (VTBN) and epoxy terminated poly(butadiene-*co*-acrylonitrile) (ETBN) were employed to improve the fracture toughness of the designed resin system. The results are summarized in Table 5 along with the fracture toughness of other commercial VE resins for comparison. The rubber modifiers used in this study did not show good miscibility with our high molecular weight, fatty acid-based FAVE-O-470HT resin system. Consequently, the toughening effect was not as good as the commercial toughened vinyl ester resins (Derakane 8084). Nonetheless, marked improvement was achieved with no loss of T_g. Our next work is to develop the appropriate modifiers needed to further improve the fracture toughness of the fatty acid based resin systems.

Table 5 Fracture toughness of liquid rubber modified and commercial VE resins

VE Resins	T _g (°C)	G _{1c} (J/m ²)
Derakane 8084	118	680
Derakane 470HT-400	173	56
FAVE-O-470HT	145	102
5 wt% ETBN FAVE-O-HT	145	135
9 wt% ETBN FAVE-O-HT	151	141
5 wt% VTBN FAVE-O-HT	146	--
9 wt% VTBN FAVE-O-HT	147	167

4. CONCLUSIONS

Novolac vinyl ester resin of Derakane 470-400 was employed in this study to improve the Tg of the fatty acid based low VOC vinyl ester resin. A dry Tg of 147°C and wet Tg of 124°C was achieved along with good processibility. Furthermore, the fracture toughness of the resulting high Tg resin is greatly improved by using liquid rubber as modifiers. However, further investigation needs to be carried out to improve the fracture toughness to a higher level.

5. ACKNOWLEDGEMENTS

The authors are thankful for support from ESTCP under project WP-0167. Moreover, the Drexel University authors acknowledge support for this work via the Army Research Laboratory Cooperative Agreement no. DAAD19-02-2-0010.

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